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# Division of Synthetic Chemistry – Organoelement Chemistry –

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## Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of fundamental chemistry, and open the way to more extensive application of main group chemistry.

### KEYWORDS

Steric Protection  
Kinetic Stabilization  
Low-coordinated Species  
Heteroatom  
Transition Metal Complexes



## Selected Publications

Mizuhata, Y.; Fujimori, S.; Sasamori, T.; Tokitoh, N., Germanbenzenylpotassium: A Germanium Analogue of a Phenyl Anion, *Angew. Chem. Int. Ed.*, **56**, 4588-4592 (2017).

Sugahara, T.; Sasamori, T.; Tokitoh, N., Highly Bent 1,3-Digerma-2-Silaallene, *Angew. Chem. Int. Ed.*, **56**, 9920-9923 (2017).

Majhi, P. K.; Ikeda, H.; Sasamori, T.; Tsurugi, H.; Mashima, K.; Tokitoh, N., Inorganic-Salt-Free Reduction in Main-Group Chemistry: Synthesis of a Dibismuthene and a Distibene, *Organometallics*, **36**, 1224-1226 (2017).

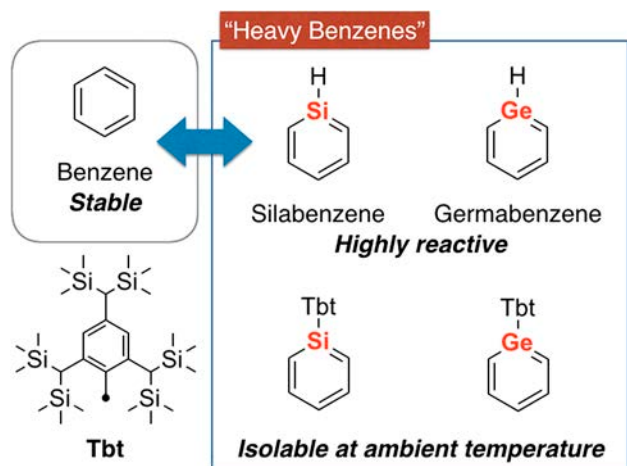
Tsunoyama, H.; Akatsuka, H.; Shibuta, M.; Iwasa, T.; Mizuhata, Y.; Tokitoh, N.; Nakajima, A., Development of Integrated Dry–Wet Synthesis Method for Metal Encapsulating Silicon Cage Superatoms of  $M@Si_{16}$  ( $M = Ti$  and  $Ta$ ), *J. Phys. Chem. C*, **121**, 20507-20516 (2017).

Kawasaki, K.; Sugiyama, R.; Tsuji, T.; Iwasa, T.; Tsunoyama, H.; Mizuhata, Y.; Tokitoh, N.; Nakajima, A., A Designer Ligand Field for Blue-Green Luminescence of Organoeuropium(II) Sandwich Complexes with Cyclononatetraenyl Ligands, *Chem. Commun.*, **53**, 6557-6560 (2017).

## Heavy Phenyl Anion

Benzene is the simplest aromatic compound and known as the basic skeleton in many organic compounds. It has been extensively studied not only from the industrial aspect such as petroleum chemistry but also the fundamental one as the most basic skeleton showing “aromaticity” since the beginning of organic chemistry.

“Heavy benzenes” in which the carbon atom(s) of the benzene ring is replaced by high-period group 14 element(s), *that is*, “heavy element” (silicon, germanium, tin, and lead), have attracted much attention from the interest of its aromaticity experimentally and theoretically. However, these compounds are extremely high-reactive species, *e.g.*, silabenzene ( $\text{HSiC}_5\text{H}_5$ ) in which one of the skeletal carbon atom of the benzene ring is replaced by a silicon atom, is known to decompose by self-oligomerization reaction even at very low temperature of  $-200^\circ\text{C}$ . We have already succeeded in the synthesis and isolation of a series of “heavy benzenes” as stable compounds even at room temperature by taking advantage of kinetic stabilization afforded by a very bulky substituent, Tbt group (see the figure), to prevent the self-oligomerization. Although these compounds are found to have “aromaticity” and unique elec-

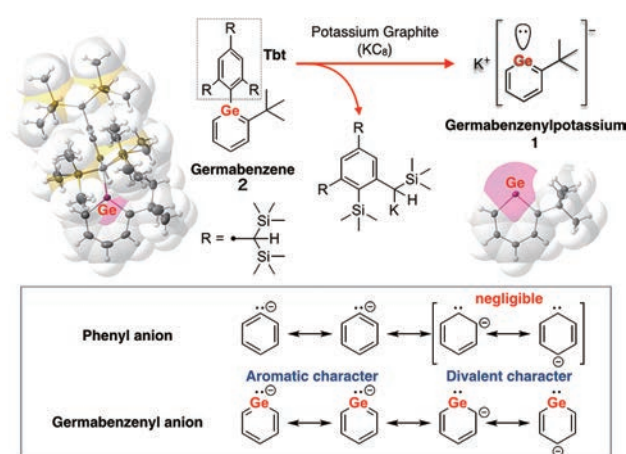


tronic state, the existence of the bulky substituent necessary for stabilization makes it difficult to develop their further applications.

In this study, we have reported the formation of germabenzenylpotassium **1** as an isolable compound together with the elimination of the Tbt group during the reduction of the stable germabenzene **2** having a Tbt group on the germanium atom and a *t*-butyl group on the adjacent carbon atom with potassium graphite ( $\text{KC}_8$ ). Compound **1** can be regarded as the anion retaining the germabenzene skeleton, *i.e.*, a germanium analog of a phenyl anion ( $\ominus\text{C}_6\text{H}_5$ ).

From both experimental and theoretical points of view, compound **1** shows not only the aromatic character but also the contribution of the canonical structure of divalent species (germylene), which is negligible in the case of phenyl anion, clearly showing the effect of substitution with germanium (heavy element).

Compound **1** can be expected as a useful reagent to introduce a germabenzene skeleton, and we have already succeeded in the synthesis of several types of new germabenzenyl derivatives. The findings of this research are expected to contribute to the design and development of novel functional molecules incorporating a germabenzene ring.



## Highly Bent “Heavy Allene”

A 1,3-digerma-2-silacyclopenta-1,2-diene, *that is*, a 1,3-digerma-2-silaallene incorporated into a five-membered ring system, was synthesized and obtained as a stable orange solid, in which the  $\text{Ge}-\text{Si}-\text{Ge}$  moiety in the planar  $\text{SiGe}_2\text{C}_2$  five-membered ring exhibited an acute angle with  $\pi$ -bonding character. On the basis of both experimental characterizations and theoretical calculations, 1,3-digerma-2-silaallene should be depicted as a  $>\text{Ge} \rightarrow \text{Si}^0 \leftarrow \text{Ge}<$  species with a pronounced  $\text{Si}^0$  character than as a  $>\text{Ge}=\text{Si}=\text{Ge}<$  heterocumulene, because of the cyclic skeleton and the strong  $\sigma$ -donating properties of the germylene moieties. Further investigations into the physical and chemical properties of such 1,3-digerma-2-silaallenes are currently in progress.

